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(54) EMULSIFIED LIPOPHILIC PAPER SIZING

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The present invention relates generally to sizing agent emulsions and to a process for the sizing of paper. More particularly, the present invention relates to novel emulsifying agents for preparing emulsions of sizing agents and for use of the emulsions in the sizing of paper and paperboard products and to the improved paper prepared therefrom.

As used herein, the terms "paper" and "paperboard" refer to sheet-like materials and molded products made from fibrous cellulosic materials and which may contain minor amounts of synthetic fibers such as polyamide, polyester and polyacrylic resin fibers, as well as mineral fibers such as asbestos and glass.

It is well known to incorporate sizing materials into paper and paperboard products for the purpose of increasing their resistance to penetration by liquids, particularly water. Unsized paper more readily absorbs liquids.

Rosin, various hydrocarbon and natural waxes, starches, sodium silicate, glues, casein, synthetic resins, rubber latex, fatty ketenes, and substituted cyclic dicarboxylic anhydrides are among the materials which have been used or have been suggested for use as sizing agents. The sizing agents may be added directly to the aqueous paper stock in a beater, or the formed paper sheet may be run through a size solution or over a roll wetted with a sizing agent. The process of sizing by the addition of a sizing agent to the paper fiber in a beater is referred to as "internal sizing". The process of sizing wherein a formed paper sheet is contacted with a sizing solution is referred to as "external sizing". The sizing agent emulsions of the present invention are useful in both internal sizing and external sizing processes.

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to provide equipment adequate to effect proper emulsification of the sizing agent. Emulsification is desirable for sizing agents so that the sizing agent is uniformly dispersed throughout the furnish in an internal sizing operation. It is desirable that the sizing agent be uniformly dispersed throughout the furnish in as small a particle size as is possible.

Accordingly, it is the principal object of the present invention to provide an emulsifying agent for use with sizing agents. It is another object of the present invention to provide sizing agent emulsions whose use results in the preparation of paper and paperboard products which are characterized by increased resistance to penetration by liquids, particularly water. A further object of the present invention is to provide emulsifying agents for use in preparing emulsions of sizing agents which emulsions may be employed with all types of paper pulp over the complete range of pH conditions which are normally encountered in paper manufacturing. A still further object of the present invention is to provide emulsifying agents which are compatible with various sizing agents and with alum and with various other components, such as fillers, pigments and other chemicals which may be added to paper.

These and other objects of the present invention will become more apparent from the following detailed description.

Generally, the emulsifying agents of the invention for use in preparing emulsions of sizing agents are selected from the group consisting of trialkyl amines wherein the alkyl moiety is methyl or ethyl and ammonium hydroxide. Particularly preferred amines for use as emulsifying agents are trimethyl amine, triethyl amine and mixtures thereof.

The emulsifying agents of the invention may be used to form aqueous emulsions of sizing agents. Preferably the aqueous emulsions herein are comprised of heterocyclic, organic

sizing agents which have at least one long hydrocarbon chain of about 8 to 30 carbon atoms attached thereto with the heterocyclic structure of said sizing agent containing an oxy group bridging two carbon atoms wherein both the carbon atoms which are attached to the oxy group contain a divalent bond, i.e., the group  . Suitable heterocyclic organic sizing agents include maleated triglycerides, maleated alpha-olefins, maleated fatty acid esters, alkyl ketene dimers, mixtures thereof and the like.

The emulsifying agents are particularly useful to form aqueous emulsions of sizing agents which comprise the reaction product of maleic anhydride and an unsaturated triglyceride oil wherein the triglyceride oil has an iodine value of at least about 50. Thus, the triglyceride oil may be partially hardened. By the term "triglyceride oil" is meant the triester of glycerol and the same or mixed fatty acids. Fatty acids refer to straight chain monocarboxylic acids having a carbon chain length of from C_8 to C_{30}.

Specific examples of such preferred sizing agents include the condensation reaction product of maleic anhydride with soy bean oil, cottonseed oil, corn oil, safflower oil, fish oil, linseed oil, peanut oil, oiticica oil, dehydrated castor oil, hempseed oil, and mixture thereof. A particularly preferred sizing agent is obtained from the reaction product of maleic anhydride and soy bean oil. Various aspects of the present invention will be hereinafter described with particular reference to the preparation of aqueous emulsions of the reaction product of maleic anhydride and soy bean oil. However, it should be understood that the emulsifying agents of the invention are suitable for use with the reaction product of maleic anhydride with other triglycerides oils and with other organic heterocyclic sizing agents.

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Although the emulsions may be used as an external sizing agent (e.g., applied to wet or dry formed paper webs), they are particularly useful as an internal sizing agent. Internal sizing is best achieved by uniformly dispersing the sizing agent throughout the fiber furnish. Dispersal of the sizing agent throughout the furnish is preferably attained by adding the sizing agent as an emulsion.

In preparing emulsions of the sizing agent, the emulsifying agent is preferably first dispersed in the sizing agent and the sizing agent is then added to the water with agitation. The sizing agent is generally present in the emulsion at a level of from about 1 to about 20 percent by weight. The trialkyl amine emulsifying agent is used at a level of from about .5 to about 2.5 percent, preferably from about 1 to about 2 percent, by weight of the sizing agent. The ammonium hydroxide is used at a level of from about .05 to about 1 percent by weight (on an ammonia basis) by weight of the sizing agent. The ammonium hydroxide is preferably used at a level of from about .1 to about .6 percent by weight of the sizing agent.

It is a surprising result of the use of the trialkyl amine and ammonium hydroxide emulsifying agents of the invention, that sizing agent emulsions can be prepared with lessened amounts and intensity of agitation. High shear agitation conditions are not required. Stable emulsions can be formed using low shear mixing conditions. As used herein the term "low shear mixing conditions" refers to the use of low shear mixing apparatus, such as a propellor mixer, operated at moderate speeds of less than about 1,500 r.p.m. This is a significant benefit of the use of the emulsifying agents of the invention, since sizing agent emulsions can be prepared with simple equipment and high capital costs are avoided.

The sizing agent emulsions of the present invention may be used in combination with a cationic agent. Cationic agents refer to materials which are capable of ionizing or dissociating in such a manner as to produce one or more cations or other positively charged moieties. Suitable cationic agents are alum, long chain fatty amines, sodium aluminate, aluminum chloride, cationic starch derivatives, polyacryl amide, chromic sulfate, and polyamide polymers. The cationic agent may be added to the furnish prior to, at the same time as, or after the addition of the sizing agent emulsion. It is preferred that the cationic agent be added either subsequent to or in direct combination with the sizing agent emulsion. However, the addition to the paper stock of either the cationic agent or the sizing agent emulsion may take place at any point in the papermaking process prior to forming the wet pulp into a dry sheet.

The sizing agent emulsions of the invention may be used for sizing of paper prepared from all types of cellulosic pulps. The cellulosic pulps which are contemplated for use include bleached and unbleached sulfite pulps, bleached and unbleached soda pulps, bleached and unbleached sulfate pulps, neutral sulfite pulp, semi-chemical pulp, chemi-ground wood pulp, ground wood pulp, and any combination of these pulps. The cellulose pulp may contain minor amounts of synthetic fibers of the polyamide, polyester, polyacrylic, viscous rayon and regenerated cellulose types.

The sizing agent emulsions of the present invention are compatible with all types of pigments and fillers which are normally used or added to the paper which is to be sized. Such materials include titanium dioxide, calcium carbonate, clay, talc, calcium sulfate, diatomaceous earths and the cationic agents previously described.

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The sizing agent emulsions of the present invention are compatible with all types of pigments and fillers which are normally used or added to the paper which is to be sized. Such materials include titanium dioxide, calcium carbonate, clay, talc, calcium sulfate, diatomaceous earths and the cationic agents previously described.

The sizing agent emulsions of the invention are used at levels sufficient to provide from about .1 to about 5 parts by weight of the sizing agent per 100 parts by weight of the cellulose pulp, dry solids basis. Preferably, from about 0.5 to about 1.5 parts by weight of the sizing agent per 100 parts by weight of pulp are used. The amount of sizing agent to be used depends upon the type of pulp which is being sized and the specific properties desired in the finished paper or paper product. Paper which requires good water resistance or ink resistance requires the use of higher concentrations of sizing agent than does paper which is used where relatively low water resistance or ink resistance is required. In general, from about 1 to about 15 parts by weight of a cationic agent are used per 5 parts by weight of sizing agent.

In preparing maleic anhydride reaction product sizing agents, the triglyceride oil, which may be partially hardened but which has an iodine value of more than 50, is first heated to a temperature in the range of from about 400°F to about 450°F. Thereafter, the maleic anhydride is added to the triglyceride oil while the triglyceride oil is being agitated to effect a condensation reaction. The maleic anhydride is maintained in contact with the triglyceride oil at the elevated temperature for a time of from about 20 minutes to about 40 minutes as the triglyceride oil is being agitated. Thereafter, the reaction mixture is permitted to cool to ambient temperature to provide the sizing agent. Oxygen and water should be excluded from the reaction mixture during the reaction. For this reason, it is preferred to blanket the surface of the triglyceride oil with an inert gas during the reaction or to conduct the reaction in a vacuum.

In general, the maleic anhydride is added to the triglyceride oil at a level of from about 0.9 to about 2 mols per

mol of triglyceride oil. At levels of addition of maleic anhydride less than the above range the resultant reaction mixture is less effective for use as a sizing agent. Higher levels of addition of maleic anhydride than the above-identified range can be used but there is no advantage to the use of such higher levels and the resultant cost of the sizing agent is increased.

The efficiency of the maleated oil sizing agents is directly related to the retention of the maleic anhydride moieties in the non-hydrolyzed form. For this reason, it is preferred that emulsions of the sizing agent have a pH of between about 5 to about 8.5. At higher or lower pH, the maleic anhydride moieties tend to hydrolyze.

The following example further illustrates various features of the present invention, but is intended to in no way limit the scope of the invention which is defined in the appended claims.

EXAMPLE I

A sizing agent emulsion in accordance with the present invention is prepared, and is used to effect sizing of a paper product. The sizing agent emulsion is used in combination with alum as a cationic agent and the water resistance of paper resulting from the use of the sizing agent is determined.

880 kgs of pure soy bean oil having an iodine value of about 125 is charged into a covered reactor. The head space in the reactor is blanketed with nitrogen. The soy bean oil is heated to a temperature of 430°F. Thereafter, maleic anhydride is added to the soy bean oil in the reactor as the soy bean oil is being agitated. The maleic anhydride is added at a level of 1.25 mols of maleic anhydride per mol of soy bean oil. The reaction mixture after the last addition of maleic anhydride is maintained at a temperature of 430°F for 30 minutes. Thereafter, the reaction mixture is allowed to cool to provide a maleated oil sizing agent.

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EXAMPLE II

Various paper samples, as set forth in Table I below were prepared using a sizing agent emulsion prepared with the emulsifying agents of the invention. In each sample, except one, the emulsifying agent is added to a maleated soy bean oil sizing agent prepared in accordance with the foregoing. In the case of sample 8, the sizing agent consisted of maleated linseed oil prepared in accordance with the foregoing procedure for preparing maleated soy bean oil. In examples 1-7, the sizing agent is maleated soy bean oil having a molar ratio of maleic anhydride to soy bean oil as set forth below in Table I. For each sample, an emulsifying agent of the invention is added to the maleated oil sizing agent. The sizing agent containing the emulsifying agent is then added to water as the water is agitated by a propeller mixer to provide an aqueous emulsion of the sizing agent. The sizing agent is added to the water at a level sufficient to provide an emulsion having 5 percent by weight of the sizing agent.

The aqueous emulsion of the sizing agent is then added to a furnish of bleached sulfite pulp having a pH of about 6.5. Alum and a quaternary amine starch derivative are previously added to the pulp. For all of the samples, except sample 1, the alum and the quaternary amine starch derivative are each present in the furnish at a ratio on a weight basis to the sizing agent of 1:1. In sample 1, alum is present at a ratio of 1.5:1 and the quaternary amine starch is present at a ratio of 1:1. The sizing agent is added to the furnish at a level sufficient to provide .5 percent by weight of the sizing agent in the furnish based on the dry weight of the pulp.

Hand sheets are formed and dried in accordance with TAPPI standards. The water resistance of the hand sheets is determined by the KBB test. In this test, the dried hand sheet is placed on an imperforate platen having an electrical lead

connected thereto. A second porous platen, also having an electrical lead connected thereto, is saturated with moisture and placed in contact with the hand sheet on the first platen. The time required to establish a current of 80 milliamps between the second platen and the first platan is measured. This time period in seconds is a measure of the effectiveness of the sizing of the paper; that is, the longer the time required to establish an 80 milliamp current, the better the water resistivity of the paper.

The following Table I sets forth data on the various hand sheets in respect to the ratio of maleic anhydride to triglyceride oil, the emulsifying agent used, the level of the emulsifying agent and the filler used, if any. In each case where a filler is used, the clay filler is used at a level of 10 percent by weight of the fiber, dry basis, and titanium dioxide is used at a level of 5 percent by weight of the fiber, dry basis.

TABLE I

Sample No.	Ratio of maleic anhydride to triglyceride oil (mols/mol)	Emulsifying agent	Level of emulsifying agent - percent by weight based on the weight of the sizing agent	Filler type	KBB test value - seconds immediately after drying	KBB test value - seconds 1 day after drying
1	1.25	NH_4OH	.33 (as NH_3)	Clay and TiO_2	50	45
2	1.25	NH_4OH	.08 (as NH_3)	None	32	35
3	1.25	Trimethylamine	.55	None	53	57
4	1.25	"	1.0	None	58	56
5	1.25	Triethylamine	1.0	Clay	66	61
6	0.5	"	1.0	Clay	13	30
7	1.5	"	1.75	Clay	34	39
8	1.25	"	1.0	Clay	44	50

connected thereto. A second porous platen, also having an electrical lead connected thereto, is saturated with moisture and placed in contact with the hand sheet on the first platen. The time required to establish a current of 80 milliamps between the second platen and the first platen is measured. This time period in seconds is a measure of the effectiveness of the sizing of the paper; that is, the longer the time required to establish an 80 milliamp current, the better the water resistivity of the paper.

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4	1.25	"	1.0	None	58	56
5	1.25	Triethylamine	1.0	Clay	66	61
6	0.5	"	1.0	Clay	13	30
7	1.5	"	1.75	Clay	34	39
8	1.25	"	1.0	Clay	44	50

EXAMPLE III

190 ml. of 110°F tap water, 10.0 g. of alkenyl succinic anhydride and 0.3 g. of triethyl amine were added to a household-type blender. An emulsion was formed by operating the blender for 1 minute. In a simular manner an emulsion of alkyl ketene dimer was prepared. Both of the aqueous emulsions were stable and were used to prepare hand sheets.

EXAMPLE IV

A sizing agent emulsion was prepared using a laboratory water aspirator attached to a water line provided with water at 60 psig pressure. A water flow rate of 18,000 ml./min. was maintained through the aspirator. A maleated soy bean oil prepared in accordance with Example I was fed through the side arm of the aspirator. The maleated soy bean oil contained 1.75 percent triethyl amine dissolved therein. A stable emulsion of the maleated soy bean oil was provided by the mixing action attained by feeding the maleated soy bean oil through the side arm of the aspirator into the stream of water flowing through the aspirator. Sufficient maleated soy bean oil was fed to the side arm of the aspirator to provide an aqueous emulsion having 1.5 percent by weight of maleated soy bean oil.

The resultant emulsion was uniformly dispersed in a paper furnish containing paper maker's alum and cationic starch in accordance with the method described in Example II. Hand sheets were made with the emulsion used as an internal sizing agent.

The level of sizing agent used, level of alum used, cationic starch level, KBB sizing value for the hand sheets produced in accordance with Examples III and IV set forth below in Table II.

TABLE II

Handsheets made by Example	Sizing Agent #/ton (dry basis)	Alum #/ton (dry basis)	Cationic Starch #/ton (dry basis)	pH	KBB Sizing-Sec.
III	10.0	10	10	6.5	91
IV	8.8	10	10	6.5	72

The emulsifying agents of the present invention are highly effective to provide emulsions of sizing agents, particularly maleated oil size agents, by simple low shear mixing. The emulsifying agent of the invention provides the paper manufacturer with an easy and effective means, requiring little capital cost, to prepare sizing agent emulsions and to utilise the sizing agent emulsions in the sizing of paper.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for providing an emulsion of a sizing agent comprising the steps of adding an emulsifying agent selected from the group consisting of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent and a sizing agent at a level of from about 1 to about 20 percent of the total emulsion weight to water to provide a mixture, and agitating said mixture to provide an emulsion.

2. A method in accordance with claim 1 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

3. A method in accordance with claim 1 wherein said emulsifying agent is ammonium hydroxide.

4. A method in accordance with claim 1, 2 or 3 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

5. A method in accordance with claim 1, 2 or 3 wherein said sizing agent is the reaction produce of maleic anhydride and an unsaturated triglyceride oil having an iodine value of at least about 50.

6. An aqueous emulsion of a sizing agent suitable for sizing paper comprising an emulsifying agent selected from the group consisting of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and

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ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent and a sizing agent at a level of from about 1 to about 20 percent of the total emulsion weight.

7. An emulsion in accordance with claim 6 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

8. An emulsion in accordance with claim 7 wherein said trialkyl amine is triethyl amine.

9. An emulsion in accordance with claim 7 wherein said trialkyl amine is trimethyl amine.

10. An emulsion in accordance with claim 6, 8 or 9 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

11. An emulsion in accordance with claim 6, 8 or 9 wherein said sizing agent is the condensation reaction product of maleic anhydride and an unsaturated triglyceride oil having an iodine value of at least about 50.

12. An emulsion in accordance with claim 6 wherein said emulsifying agent is ammonium hydroxide.

13. A method for internal sizing of paper comprising adding to paper furnish an emulsion comprising a sizing agent at a level of from about 1 to about 20 percent of the total emulsion weight and an emulsifying agent selected from the group comprising of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent.

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ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent and a sizing agent at a level of from about 1 to about 20 percent of the total emulsion weight.

7. An emulsion in accordance with claim 6 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

8. An emulsion in accordance with claim 7 wherein said trialkyl amine is triethyl amine.

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10. An emulsion in accordance with claim 6, 8 or 9 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

11. An emulsion in accordance with claim 6, 8 or 9 wherein said sizing agent is the condensation reaction product of maleic anhydride and an unsaturated triglyceride oil having an iodine value of at least about 50.

12. An emulsion in accordance with claim 6 wherein said emulsifying agent is ammonium hydroxide.

13. A method for internal sizing of paper comprising adding to paper furnish an emulsion comprising a sizing agent at a level of from about 1 to about 20 percent of the total emulsion weight and an emulsifying agent selected from the group comprising of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent.

14. The method of claim 13 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

15. The method of claim 14 wherein said trialkyl amine is triethyl amine.

16. The method of claim 14 wherein said trialkyl amine is trimethyl amine.

17. The method of claim 13, 15 or 16 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

18. The method of claim 13 wherein said sizing agent is the condensation reaction product of maleic anhydride and an unsaturated triglyceride oil having an iodine value of at least about 50.

19. The method of claim 18 wherein said emulsifying agent is ammonium hydroxide.

20. The method of claim 19 wherein said ammonium hydroxide is present in said emulsion at a level of from about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent.

21. A method for preparing an internal paper sizing emulsion which comprises adding at a level of from about 1 to about 20 percent of the total emulsion weight, a water-insoluble, non-hydrolyzed, heterocyclic sizing agent characterized as having at least one long hydrocarbon chain of about 8 to 30 carbon atoms with the heterocyclic structure of said sizing agent containing an oxy group bridging two carbon atoms wherein both the carbon atoms which are attached to the oxy group contain a

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divalent bond, and an emulsifying agent selected from the group consisting of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent to water at a pH between about 5.0 to about 8.5 to provide a mixture, and agitating said mixture to provide said emulsion wherein said sizing agent is uniformly dispersed and emulsified in said water by said emulsifying agent.

22. The method in accordance with claim 21 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

23. A method in accordance with claim 21 wherein said emulsifying agent is ammonium hydroxide.

24. A method in accordance with claim 21 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

25. A method in accordance with claim 24 wherein said sizing agent is the reaction product of about 0.9 to about 2 moles maleic anhydride and one mole of unsaturated triglyceride oil, the non-hydrolyzed reaction product has an iodine value of at least about 50 and the internal paper sizing emulsion is uniformly dispersed throughout a cellulose paper furnish in an amount, on a dry solids weight basis, ranging from about 0.5 to about 1.5 parts by weight reaction product for each 100 parts by weight cellulose pulp.

26. An aqueous emulsion of a sizing agent suitable for sizing paper comprising a water-insoluble, non-hydrolysed, heterocyclic sizing agent characterised as having at least one

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divalent bond, and an emulsifying agent selected from the group consisting of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent to water at a pH between about 5.0 to about 8.5 to provide a mixture, and agitating said mixture to provide said emulsion wherein said sizing agent is uniformly dispersed and emulsified in said water by said emulsifying agent.

22. The method in accordance with claim 21 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine.

23. A method in accordance with claim 21 wherein said emulsifying agent is ammonium hydroxide.

24. A method in accordance with claim 21 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

25. A method in accordance with claim 24 wherein said sizing agent is the reaction product of about 0.9 to about 2 moles maleic anhydride and one mole of unsaturated triglyceride oil, the non-hydrolyzed reaction product has an iodine value of at least about 50 and the internal paper sizing emulsion is uniformly dispersed throughout a cellulose paper furnish in an amount, on a dry solids weight basis, ranging from about 0.5 to about 1.5 parts by weight reaction product for each 100 parts by weight cellulose pulp.

26. An aqueous emulsion of a sizing agent suitable for sizing paper comprising a water-insoluble, non-hydrolysed, heterocyclic sizing agent characterized as having at least one

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long hydrocarbon chain of about 8 to 30 carbon atoms attached thereto with the heterocyclic structure of said sizing agent containing an oxy group bridging two carbon atoms wherein both the carbon atoms which are attached to the oxy group contain a divalant bond, said sizing agent being present at a level of from about 1 to about 20 percent of the total emulsion weight, and said sizing agent being emulsified with an emulsifying agent selected from the group consisting of a trialkyl amine at a level of from about 0.5 to about 2.5 percent by weight of said sizing agent and ammonium hydroxide at a level of from about 0.05 to about 1 percent by weight, on an ammonia basis, by weight of said sizing agent.

27. The emulsion in accordance with claim 26 wherein said trialkyl amine is triethyl amine.

28. The emulsion in accordance with claim 26 wherein said trialkyl amine is trimethyl amine.

29. The emulsion in accordance with claim 26, 27 or 28 wherein said sizing agent is selected from tne group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers.

30. The emulsion in accordance with claim 26, 27 or 28 wherein said sizing agent is the condensation reaction product of about 0.9 to about 2.0 moles maleic anhydride and one mole unsaturated triglyceride oil and the reaction product has an iodine value of at least about 50 and the internal paper sizing emulsion is uniformly dispersed throughout a cellulosic paper furnish (on a dry solids weight basis) in an amount ranging from about 0.5 to about 1.5 parts by weight reaction product for each 100 parts by weight cellulose pulp.

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31. A method for internal sizing of paper comprising adding to a cellulose pulp an internal paper sizing emulsion having a pH between about 5.0 to about 8.5, said emulsion comprising water, emulsifying agent and a water-insoluble, non-hydrolyzed, heterocyclic sizing agent at a level from about 1 to about 20 percent of the total emulsion weight, said heterocyclic sizing agent being characterized as having at least one long hydrocarbon chain of about 8 to 30 carbon atoms attached thereto with the heterocyclic structure of said sizing agent containing an oxy group bridging two carbon atoms wherein both the carbon atoms which are attached to the oxy group contain a divalent bond and the emulsifying agent for said sizing agent is selected from the group consisting of a trialkyl amine at a level from about 0.5 to about 2.5 percent of the sizing agent weight and ammonium hydroxide at a level of about 0.05 to about 1 percent, (on an ammonia weight basis), of said sizing agent weight to provide an internally sized paper furnish, and converting said furnish to a dry, internally sized paper product.

32. The method of claim 31 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine and the internal paper sizing emulsion is added to the paper furnish at a level ranging from about 0.1 to about 5 parts by weight sizing agent for each 100 parts by weight of the cellulose pulp.

33. The method of claim 32 wherein said trialkyl amine is present in said emulsion at a level of from about 1 to about 2 percent by weight of said sizing agent.

34. The method of claim 33 wherein said trialkyl amine is triethyl amine.

35. The method of claim 33 wherein said trialkyl amine is trimethyl amine.

31. A method for internal sizing of paper comprising adding to a cellulose pulp an internal paper sizing emulsion having a pH between about 5.0 to about 8.5, said emulsion comprising water, emulsifying agent and a water-insoluble, non-hydrolyzed, heterocyclic sizing agent at a level from about 1 to about 20 percent of the total emulsion weight, said heterocyclic sizing agent being characterized as having at least one long hydrocarbon chain of about 8 to 30 carbon atoms attached thereto with the heterocyclic structure of said sizing agent containing an oxy group bridging two carbon atoms wherein both the carbon atoms which are attached to the oxy group contain a divalent bond and the emulsifying agent for said sizing agent is selected from the group consisting of a trialkyl amine at a level from about 0.5 to about 2.5 percent of the sizing agent weight and ammonium hydroxide at a level of about 0.05 to about 1 percent, (on an ammonia weight basis), of said sizing agent weight to provide an internally sized paper furnish, and converting said furnish to a dry, internally sized paper product.

32. The method of claim 31 wherein said emulsifying agent is a trialkyl amine selected from the group consisting of trimethyl amine and triethyl amine and the internal paper sizing emulsion is added to the paper furnish at a level ranging from about 0.1 to about 5 parts by weight sizing agent for each 100 parts by weight of the cellulose pulp.

33. The method of claim 32 wherein said trialkyl amine is present in said emulsion at a level of from about 1 to about 2 percent by weight of said sizing agent.

34. The method of claim 33 wherein said trialkyl amine is triethyl amine.

35. The method of claim 33 wherein said trialkyl amine is trimethyl amine.

36. The method of claim 31 wherein said sizing agent is selected from the group consisting of maleated triglycerides, maleated alpha-olefins, maleated fatty esters, and alkyl ketene dimers and the heterocyclic sizing agent is added to the paper furnish in an amount (based on the dry solids weight) ranging from about 0.1 to about 5.0 parts by weight heterocyclic sizing agent for each 100 parts by weight cellulose pulp.

37. The method of claim 36 wherein said sizing agent is the condensation reaction product of about 0.9 to about 2 moles maleic anhydride and one mole of unsaturated triglyceride oil and the reaction product has an iodine value of at least about 50.

38. The method of claim 37 wherein said emulsifying agent is ammonium hydroxide.

39. The method of claim 38 wherein said ammonium hydroxide is present in said emulsion at a level of from about 0.1 to about 0.6 percent by weight, on an ammonia basis, by weight of said sizing agent.